

# UNPUBLISHED PRELIMINARY DATA

Project AD-1689-A

CORNELL AERONAUTICAL LABORATORY, INC.

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## NONEQUILIBRIUM GASDYNAMICS RELATED TO PROPULSION SYSTEMS

Contract NASr-109

QUARTERLY REPORT for period ending

31 March 1965

### 1. INTRODUCTION

During the past quarter the research performed under Nonequilibrium Gasdynamics, Contract NASr-109, has concentrated on the following areas:

- (1) Preparation of a report on theoretical studies of catalysis of hydrogen-atom recombination,
- (2) Preparation of a report on the machine computer code for the numerical solution of the inviscid streamtube flow of a reacting mixture,
- (3) Theoretical studies of vibrational nonequilibrium and vibration-recombination coupling in nozzle-expansion flows,
- (4) Study of impurity effects on vibrational relaxation of nitrogen, using the spectrum line reversal method, and
- (5) Further development of the technique of spectroscopically following atomic concentrations in shock-wave flows.

A report on the theoretical gas-phase catalysis studies<sup>1</sup> has been written and is now being prepared for publication. Preparation of the report on the machine computer code is about 75 per cent completed. The NASA Contractor's

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Meeting, March 16-19, was attended and the spectrum line reversal studies were discussed in detail at that meeting.

## 2. THEORETICAL GAS-PHASE CATALYSIS STUDIES

In an earlier investigation under this contract nonequilibrium nozzle flow solutions were obtained for the hydrogen-carbon system.<sup>2</sup> The results of these studies showed that marginal gains in the performance of hydrogen rockets could be achieved by adding trace amounts of carbon. During the present contract period gas-phase catalysis studies of the use of oxygen and oxygen-nitrogen mixtures as additives have been completed. Both the earlier work and the present investigation have shown that the success of the increase in hydrogen-atom recombination rate in overcoming the molecular-weight penalty of the additive depends critically on the reaction-rate values employed for the catalytic mechanisms. The results of both the earlier studies and the recent calculations have been employed to generate minimum requirements which any additive must satisfy to yield a gain in rocket specific impulse. Also, the results of both sets of calculations are used to show that, although gas-phase catalysis may not yield large percentage gains in specific impulse, it may lead to significant savings in tankage weight. A detailed report has been written on all of these aspects of the gas-phase catalysis study and at present is being prepared for publication.<sup>1</sup>

## 3. STREAMTUBE PROGRAM REPORT

A computer program has been developed at CAL for the numerical solution of one-dimensional, inviscid flows of multicomponent reacting mixtures.<sup>3</sup> The technique of solution has been developed to the point where this program is a useful tool for studying nonequilibrium flow in wind tunnel and rocket nozzles

and for designing kinetics experiments in such flows. Under the present contract a report is being prepared<sup>4</sup> which describes the program and contains instructions on its use. This report is intended to accompany the Fortran-language program cards and hence makes the program available to others. A detailed outline of the report has been given in preceding progress reports. At this time about 75 per cent of the report has been written and it will be completed in the near future.

#### 4. VIBRATIONAL NONEQUILIBRIUM AND VIBRATION-RECOMBINATION COUPLING STUDIES

The effort under this part of the contract has been concerned with vibrational relaxation effects on expanding flows. The basic approach has been to treat each vibrational level, or group of levels, as a separate chemical species.<sup>5</sup> Transitions between vibrational levels then occur as chemical reactions among the "species". This model thus permits use of the computer program developed for chemical nonequilibrium studies<sup>3, 4</sup> to investigate vibrational nonequilibrium. The work on this aspect of the nozzle flow has closely followed corresponding studies<sup>6</sup> of shock-wave flows under Contract NASr-119.

One of the problems that has been studied with this model is the vibrational relaxation in nozzle flows of dilute nitrogen-argon mixtures. Experiments performed on such flows<sup>7</sup> indicate that the vibrational relaxation times in expanding flows are much shorter than those measured in shock-wave flows. One of the features of the vibrational model used in the present study was that the transition probabilities for the upper levels were higher than those for a simple harmonic oscillator. A nozzle-flow computation was carried out for an expansion of a 1% N<sub>2</sub> in argon mixture from reservoir conditions of 4000°K and 100 atm.

The solution indicated a frozen vibrational temperature to be lower ( $\sim 2700^\circ\text{K}$ ) than predicted using harmonic oscillator transition probabilities ( $\sim 3100^\circ\text{K}$ ). However, the calculated value was not as low as the measured value ( $\sim 2000^\circ\text{K}$ ). This result does not necessarily invalidate the vibrational model, since the shock-tube data on vibrational relaxation have thus far not been compared with a computation based on the present model. Such a comparison may lead to revised relaxation times that could improve the agreement between theory and experiment.

The above model for the vibrational degree of freedom has also been employed to study vibration-recombination coupling in nozzle flows. In addition to assuming higher transition probabilities for upper vibrational states, the rate of recombination into these upper states is also assumed to be more efficient than that of an harmonic oscillator. A solution for the nozzle expansion of a dissociated oxygen-argon mixture has been attempted. As a consequence of the model the upper vibrational states remain very near a local equilibrium. Even with the improved integration scheme currently used in the program the computation is consequently prohibitively long. Thus, before completing this study an alternative integration scheme is needed. One possibility is to combine a linearization procedure such as suggested in Ref. 8 with the modified Runge-Kutta method now used.

## 5. SPECTRUM-LINE REVERSAL STUDIES

Detailed studies of the effects of controlled amounts of added impurities on the line-reversal temperatures measured in  $\text{N}_2$  expansion flows were completed during the past quarter. In these studies, trace amounts of  $\text{C}_2\text{H}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  were premixed with the  $\text{N}_2$  test gas before introduction into the

shock tube. During each run the emission spectrum of the test gas was monitored in the reflected shock region with a small-dispersion prism spectrograph to verify the presence of molecular impurities in the test gas prior to expansion in the nozzle. Simultaneously, time-resolved line reversal measurements of the Na excitation temperatures were obtained at a nozzle area ratio of  $A/A^*=8$ .

The initial impurity content in the pre-shocked test gas in these experiments was varied from about 100 to 10,000 PPM. The measurements were performed for reservoir temperatures of 3200°K and 4250°K and for a reservoir pressure of about 50 atm. The results of these measurements indicate a threshold value of about 1000 PPM of impurity below which no effect on the reversal temperature is observed. For larger impurity content, the data indicate a systematic reduction in the observed Na excitation temperatures indicative of a faster rate of  $N_2$  vibrational de-excitation.

The largest effect at the reservoir temperature of 4250°K was obtained with  $C_2H_2$  additive which indicated a reduction in the reversal temperature of about 150°K for an initial concentration of 3000 PPM. At this reservoir temperature the addition of 3000 PPM of  $O_2$  impurity resulted in about a 70°K reduction while the effect of  $CO_2$  was essentially negligible. At the lower reservoir temperature of 3200°K, the addition of  $O_2$  up to 3000 PPM yielded no observable effect. The addition of  $CO_2$  and  $C_2H_2$  yielded similar results, indicating a reduction in the reversal temperature of about 60°K for an initial concentration of about 3000 PPM. The addition of water vapor caused the largest effect at this reservoir temperature. This effect amounted to a reduction of the reversal temperature of about 100°K for an initial impurity content of 3000 PPM. (The effect of water vapor at the higher reservoir temperature of 4250°K was

not investigated since it was anticipated that  $H_2O$  would be almost completely dissociated at that temperature.)

The results of these studies clearly indicate that "normal" impurity content (  $< 100$  PPM) of the nonequilibrium nozzle flow experiments is well below the values at which any impurity effects may be significant. The sensitivity of the experimental technique for obtaining these results insures that at the normal levels, impurities do not exert any direct influence of the Na excitation or indirectly via the molecular vibrational mode.

## 6. ATOMIC SPECTROPHOTOMETRIC STUDIES

Initial observations have now been made with the recently completed CAL high-purity shock tube. The tube and associated spectrophotometric apparatus for observing the Lyman -  $\alpha$  absorption of the hydrogen atom have been completed and assembled. However, a thorough check for leaks indicated that several metallic O-ring seals required improved machining.

Before the apparatus was disassembled for elimination of these leaks, a number of shock tube observations were made in order to test the over-all capability of the new system. The results were most gratifying. With a leakage rate comparable to that of the old tube, essentially the same rate of formation of atomic hydrogen was measured. However, with approximately the same electronic-filter time constant as before ( $8 \mu$  sec), the new signal-to-noise ratio was roughly 600% better. This can be attributed to three principal factors:

- (1) Elimination of the one-meter-long reflection path between the shock tube and spectrometer;
- (2) substitution of a new technique for focussing the vacuum UV radiation on

(2) continued

the photomultiplier, consisting of coating an aluminum mirror with the fluorescent compound, instead of coating the PM tube;

- (3) cooling the PM to dry-ice temperature. With these improvements, the kinetic trace is virtually a smooth curve. The accuracy of the data should thus be adequate for interpretation of the results in terms of reaction mechanisms.

After the completion of these initial runs, the seals causing leakage have been taken out for modification. After re-sealing, efforts will begin to attain ultimate vacuum conditions. Further runs will be performed prior to baking. Final baking is awaiting arrival of special washers to take up any deterioration of bolt tensions caused by uneven expansions and contractions during the heating cycles.

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